

THE SWELLING MECHANISM OF CATHODES
IN $\text{Li}/(\text{CFx})_n$ CELLS

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ABSTRACT

Active material particles spatial arrangement in combination with the nature of the electrochemical reduction mechanism were found to be the major cause of excessive swelling in cathodes in $\text{Li}/(\text{CFx})_n$ cells. A better understanding of the chemical reaction mechanism, a possible new role for the carbon and a model for cathode growth are discussed.

INTRODUCTION

Early developers of lithium-organic electrolyte cells were attracted to $(\text{CFx})_n$ as a potential cathode material. This attraction was based on calculated theoretical energy values of which the most outstanding was a theoretical specific energy approaching 2000 wh/kg*. Calculations of solid volume changes in the $\text{Li}/(\text{CFx})_n$ cells, based on "crystallographic" densities, indicated a volume reduction caused by active materials transforming into products of about 35%. However, in practice, loading of active materials was limited by an unexplained severe cathode swelling which resulted in cell choking and/or bulging of flat cell walls.

This investigation was aimed at trying to understand the cathode swelling phenomenon and, if possible, find a way to increase the active material loading in $\text{Li}/(\text{CFx})_n$ cells.

The results of the first part of this project were reported in the 1990 NASA Aerospace Battery Workshop. This presentation covers a review of the early results, new insight into the role of carbon in the cathode reaction mechanism, a swelling model based on microscopic observation and cells swelling behavior and conclusion.

* This number is based on the assumption that the EMF of the electrochemical reaction is between 2.8 and 2.9 volts. See - J. P. Gabano, "An Overview" in "Lithium Batteries" (J. P. Gabano ed) P. 2, Academic Press, New York, NY, 1983.

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VOLUME CHANGES OF CATHODES IN BR-2325 CELLS DUE TO DISCHARGE

WET CATHODES VOLUME BEFORE DISCHARGE

	Volume *(Cm ³)
PC/DME	0.261
GBL	0.251

CATHODES FROM DISCHARGED CELLS

32°F and 120°F Discharge Across a 37,500 ohm Load

Δ Volume* (%)

	<u>32°F</u>	<u>120°F</u>
PC/DME	36	1
GBL	36	2

75°F Discharge Across a 15,000 ohm Load

Δ Volume* (%)

PC/DME	27
GBL	28

* \pm 1%

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APPROACH

The problem is illustrated by the data obtained from measurements performed on cathodes from fresh and discharged BR-2325 cells.

Approximately doubling of electrodes volume was reported for experiments conducted with essentially free "standing" electrodes.* That report indicated that no temperature effect was observed with the highly porous "free standing" electrodes.

Initially, the source of the problem was thought to be related to the reaction mechanism, hence the prevailing mechanism for the electrode reduction required a careful review.

As no mechanistic answer on the atomic level could explain the observed magnitude of electrode swelling, microscopic observations of active cathode material particles behavior during discharge were investigated in search for an explanation for the excessive growth.

Finally, an atomic-microscopic model was evolved which can explain the observed swelling phenomenon.

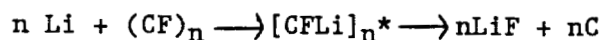
* D.M. Pasquariello, E.B. Willstaedt and K.M. Abraham, The Electrochemical Society, Fall Meeting, Paper No. 17, Seattle, Washington, October 1990.

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ELECTROCHEMICAL REDUCTION OF PTFE AND $(CF_x)_n$ BY LITHIUM

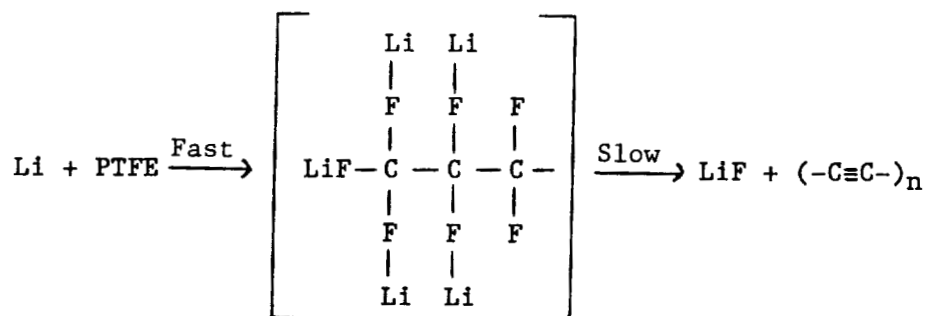
PROPOSED MECHANISMS

$(CF_x)_n$



* Prevailing literature intermediate $[CF \cdot Li(S)_n]$

PTFE (Dousek et al)



$[-C \equiv C-]_n \longrightarrow$ to more ordered form

$LiF \longrightarrow$ to larger crystals

PROBLEM:

In both cases x-ray diffraction patterns do not show intermediate; hence

HOW DOES THE LITHIUM REACH REACTION SITES?

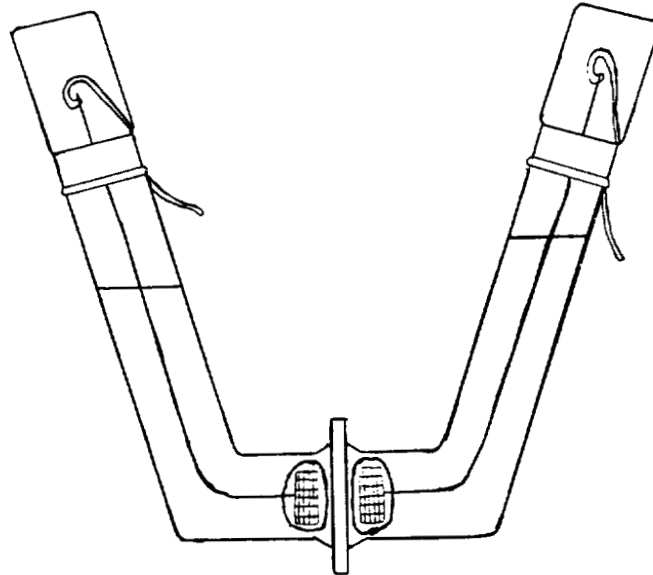
ROLE OF CARBON

(Reaction Mechanism)

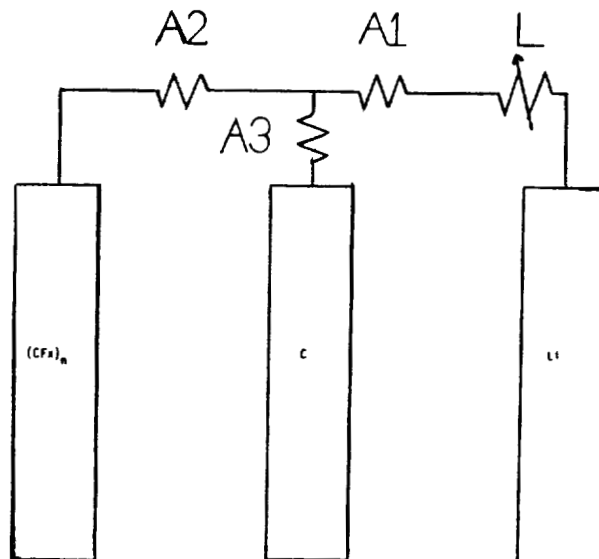
Reaction mechanisms proposed, in the literature, for the $(CF_x)_n$ electrode reduction by lithium assume lithium ion penetration to reaction sites between layers of active material via an intermediate. A similar mechanism is proposed for the reduction of PTFE by lithium metal.

X-ray diffraction patterns show only the presence of LiF on both reduction products and disordered carbon on the surface of discharged $(CF_x)_n$ particles. Hence, lithium has to penetrate the discharging active material particles in both cases through the discharge products as complete disintegration of particles down to the "molecular" level was not observed.

Based on carbon intercalation chemistry literature, which is abundant, and the expected slow lithium ion diffusion through LiF crystals, we proposed last year that lithium could be first "intercalated" into the discharged carbon and then proceed to $(CF_x)_n$ sites. Experiments designed to verify the proposed lithium migration path gave interesting results.



"Lithium passage through carbon" cell.



Schematic Drawing of the "lithium passage through carbon" experimental setup.

- A1 - Resistor used to measure total current flow.
- A2 - Resistor used to measure current flow to $(CFx)_n$.
- A3 - Resistor used to measure current flow to carbon.
- L - Resistive load controlling current flow.

ROLE OF CARBON

(Experimental)

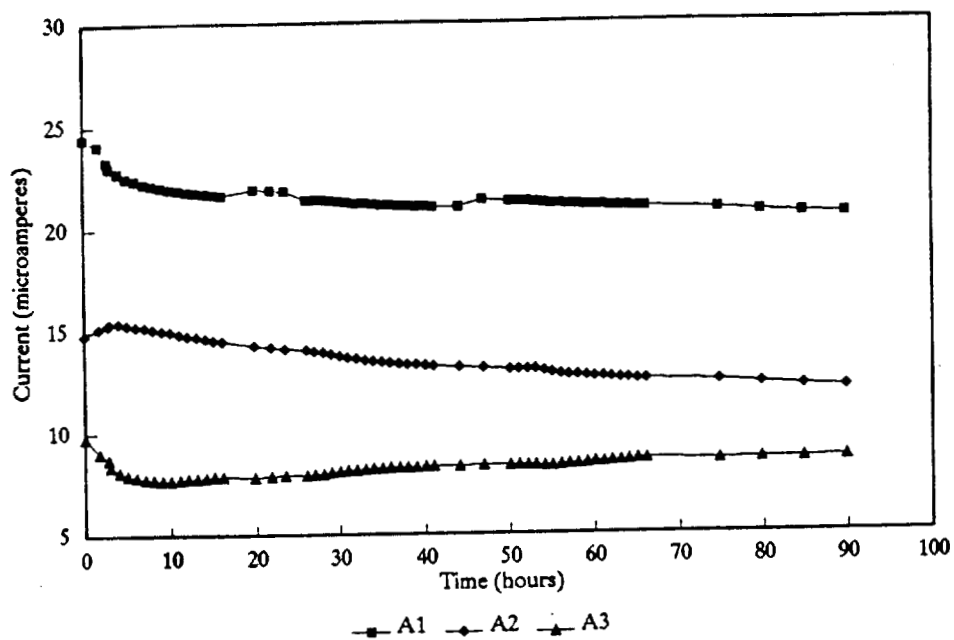
The experimental setup designed to understand the role of carbon in the cathode reaction consisted of a Li/Li salt in an organic solvent/ $(CF_x)_n$ cell separated into two compartments by a piece of Pyrolytic Graphite - Coated Graphite (Pyrotech, PT101).

This cell was discharged through a large resistance, L and the currents flowing from the lithium, to the carbon and to the $(CF_x)_n$ electrodes were measured through smaller calibrated resistors A1, A3 and A2, respectively, using DVMs. The voltage between the two electrodes, Li and $(CF_x)_n$ was also monitored during the experiments.

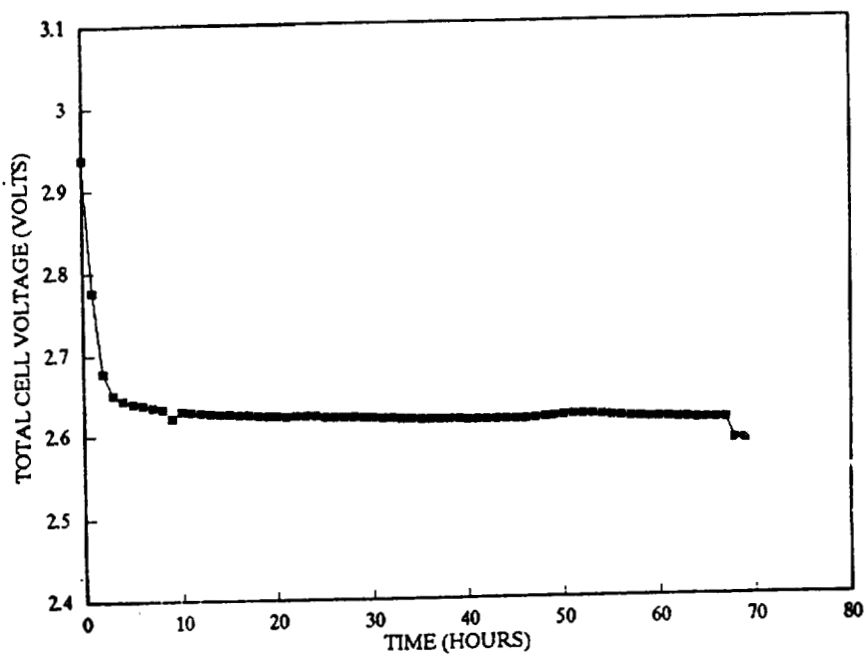
Initial results with a $1MLiAsF_6$ in DMSI solution indicated no current flow through A2 unless the carbon was loaded with some lithium. Loading the carbon, by disconnecting A2, and unloading the carbon, by disconnecting A1, resulted in increasing and decreasing the ability of the cell to deliver current at several predesigned discharge voltages indicating limits on cell performance dependent on lithium presence in the carbon.

However, gas formation was detected in the positive electrode compartment as the experimental work progressed. Consequently, the experiments were repeated with a $1MLiAsF_6$ in PC.

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Current distribution for cell B at the start of loading.
(Load @ 102K ohm)



Cell A - Total cell voltage, vs. time, for
beginning of loading (first run load @ 200K).

ROLE OF CARBON

(Results)

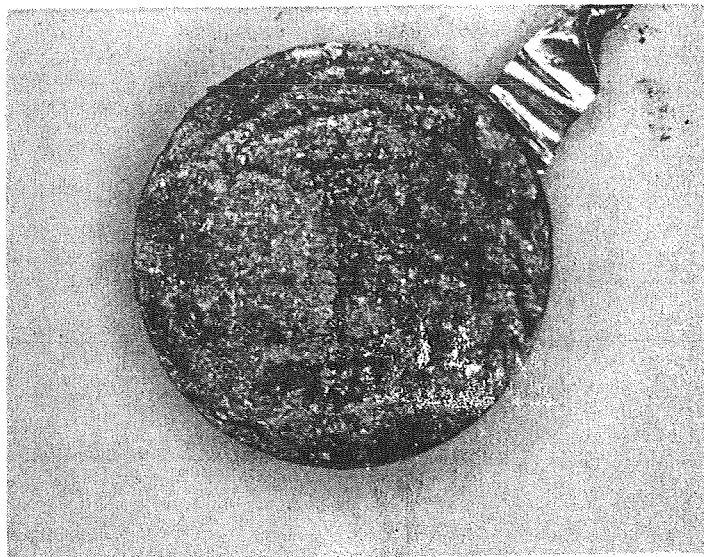
Results obtained with the PC solution varied some with the piece of carbon used. In the case of one cell similar results to those obtained with DMSI were obtained.

However, more interesting were results which were obtained with, what could be assumed to be, not completely sealed surfaces of the carbon. With such slightly open faced pieces current started flowing ~~in both~~ to both the carbon and the $(CFx)_n$ with the sum of the currents equal, within the measuring accuracy (two significant figures), to that flowing from the lithium electrode. Furthermore, current was flowing to the carbon even as the cell voltage was significantly above 2 volts.

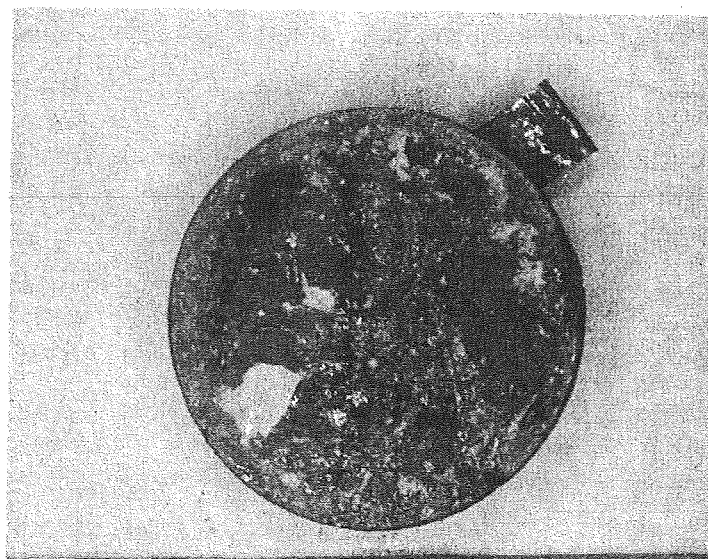
Such behavior indicates carbon loading with lithium while the cell is discharging. Hence, if one assumes that $(CFx)_n$ is fully covered with discharge product, even if slightly cracked, then the observed discharge voltages could be attributed to mixed potentials involving lithium loading on carbon and its ultimate reaction with the positive active material.

Attributing an ionic current conducting role to carbon in the cathode reaction could account for some positive electrode swelling due to lithium presence in carbons in the $(CFx)_n$ electrode, i.e., both the discharge product and the conductive additive.

Still the observed magnitude of swelling cannot be explained in terms of the carbon-lithium reaction above.



a. Cathode pellet after some scraping of adherent materials.



b. Cathode pellet after intensive scraping.

Current collecting surfaces of pellets from PC test tube
cells after discharge.

MICROSCOPIC OBSERVATION

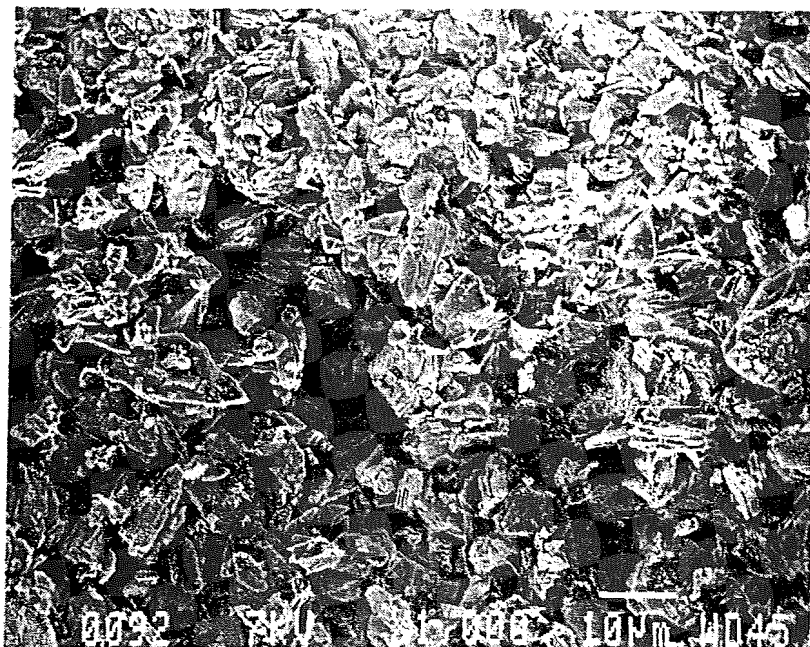
Visual and microscopic examination of specially made "electrodes" gave better insight into the swelling mechanism.

These electrodes consisted of a pellet made from shiny high purity graphite powder on which gray $(\text{CFx})_n$ powder was sprinkled and allowed to discharge slowly vs lithium (CCV 1.8 volts) under flooded conditions in a 1M LiAsF_6 in PC solution.

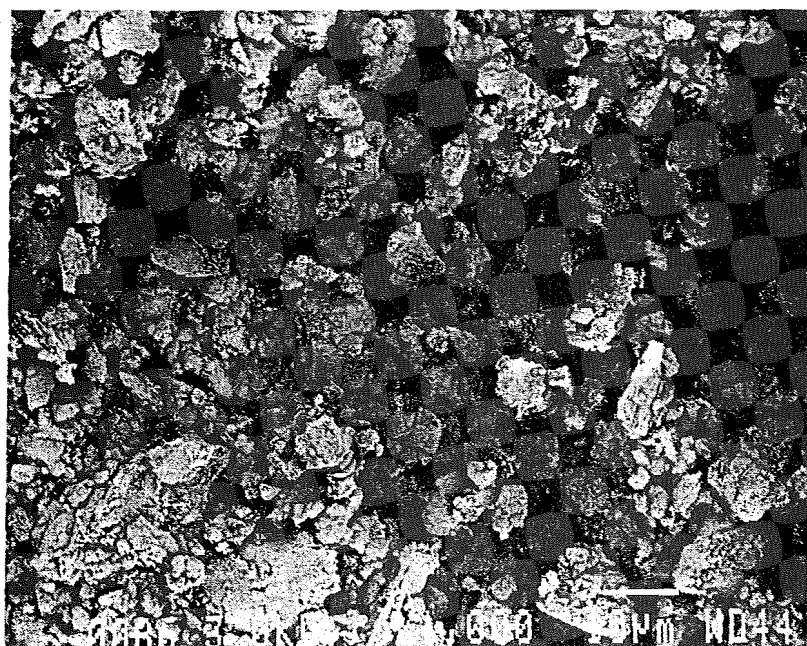
Surprisingly, partially discharged material on the surface of these electrodes hardened into a porous matrix and had to be scraped for further observation. Scraping of such partially discharged electrodes revealed a gray upper layer of partially discharged material on the top of the electrode and a dull black layer on top of the shiny graphite surface of the pellet.

Further examination of the layers revealed that even the partially discharged particles were fused together allowing for sizable pores between particles. Some shrinkage of particles, but not the disappearing of cavities, was observed with the dark material.

Furthermore, in all cases the fused active material particles were fused also to the graphite.



a. Gray surface.



b. Black surface.

SEM micrographs of the gray and black surfaces on a scraped current collecting surface of the graphite pellet from cell LT 2.

SWELLING MODEL

Based on the above, a reasonable model for $(\text{CFx})_n$ cathode swelling will consist of the following steps:

1. Electrons reach $(\text{CFx})_n$ particles' surfaces through the conductive additive - carbon, and lithium ions reach reaction sites via solution.
2. Reaction taking place at sites of least resistance, e.g., the conductive carbon surface, resulting in fusion of discharging particles to the carbon.
3. The reaction proceeds by advancing through partially discharged particles to undischarged particles which touch them resulting in particles fusion at touching surfaces before full reduction of the fused particles.
4. Any further reduction of the fused particles matrix which results in particle swelling, i.e., incorporation of lithium in carbon, LiF crystal formation and further layer separation will result in amplified three dimensional swelling around the fused matrix cavities.
5. Such swelling will continue unimpeded in free standing electrodes but will be limited if the electrode is swelling against a solid metal wall. In the latter case the wall pressure could result in particle matrix breakage and densification resulting in less bulging and cell chocking.

One could also expect the matrix-wall interaction to be more sensitive to temperature than the swelling of a free standing electrode.

CONCLUSIONS

The major contributor to cathode swelling in $\text{Li}/(\text{CFx})_n$ cells is the formation and three dimensional expansion of the fused particle matrix.

Lithium reaction with carbon in the $(\text{CFx})_n$ electrode provides for an acceptable explanation for lithium ion migration during discharge and might explain observed voltages during discharge.

ACKNOWLEDGEMENT

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